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# Supporting Information

## Direct Analysis of Metal Ions in Solutions with High Salt Concentrations by Total Reflection X-ray Fluorescence (TXRF)

Mercedes Regadío, Sofía Riaño, Koen Binnemans, and Tom Vander Hoogerstraete\*

KU Leuven - University of Leuven, Department of Chemistry, Celestijnenlaan 200F, 3001 Heverlee (Belgium)

**Corresponding Author.** \*Tom Vander Hoogerstraete, KU Leuven, Department of Chemistry, Celestijnenlaan 200F, P.O. Box 2404, B-3001 Heverlee (Belgium). [Tom.Vanderhoogerstraete@kuleuven.be](mailto:Tom.Vanderhoogerstraete@kuleuven.be).

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### Calculation of the Sensitivity factors after calibration of the TXRF spectrometer S2 PICOFOX™ molybdenum.

The sensitivity factors ( $S_i$ ) were calculated according to the Eq. (S1), where  $C_{IS}$  is the concentration of the internal standard (100 mg L<sup>-1</sup> of gallium),  $N_i$  is the net pulse number of counts in the measured spectrum of the analyte  $i$  (counts),  $S_{IS}$  is the relative sensitivity of the internal standard element (1 by convention),  $N_{IS}$  is the net pulse number in the measured spectrum of the internal standard (counts) and  $C_i$  is the measured concentration of the analyte  $i$ . The input data came from measuring 10 calibration solutions in duplicate, which were equally prepared two by two; i.e., five different calibration points. These calibration solutions consisted of multi-element standards containing in all the solutions 100 mg L<sup>-1</sup> of gallium and in each one of the calibration solutions 5, 15, 50, 100 or 200 mg L<sup>-1</sup>, respectively. Therefore, the calculated  $S_i$  were obtained by a 4-data average for each five calibration point. All measurements lasted for 1000 s.

$$S_i = \frac{C_{IS} \cdot N_i \cdot S_{IS}}{N_{IS} \cdot C_i} \quad (S1)$$

As part of the calibration, the elemental concentrations obtained after measuring ( $C_i$ ) were normalized ( $C_{Ni}$ ) by dividing them by a correction factor, calculated as the average concentration of the analyte measured in the corresponding blanks ( $C_B$ ) divided by the calculated theoretical concentration of the analyte ( $C_{T,B}$ ) (Eq. S2).

$$C_{Ni} = \frac{C_i}{C_B / C_{T,B}} \quad (S2)$$

TXRF spectra that depict the number of counts vs. the characteristic energy of each element

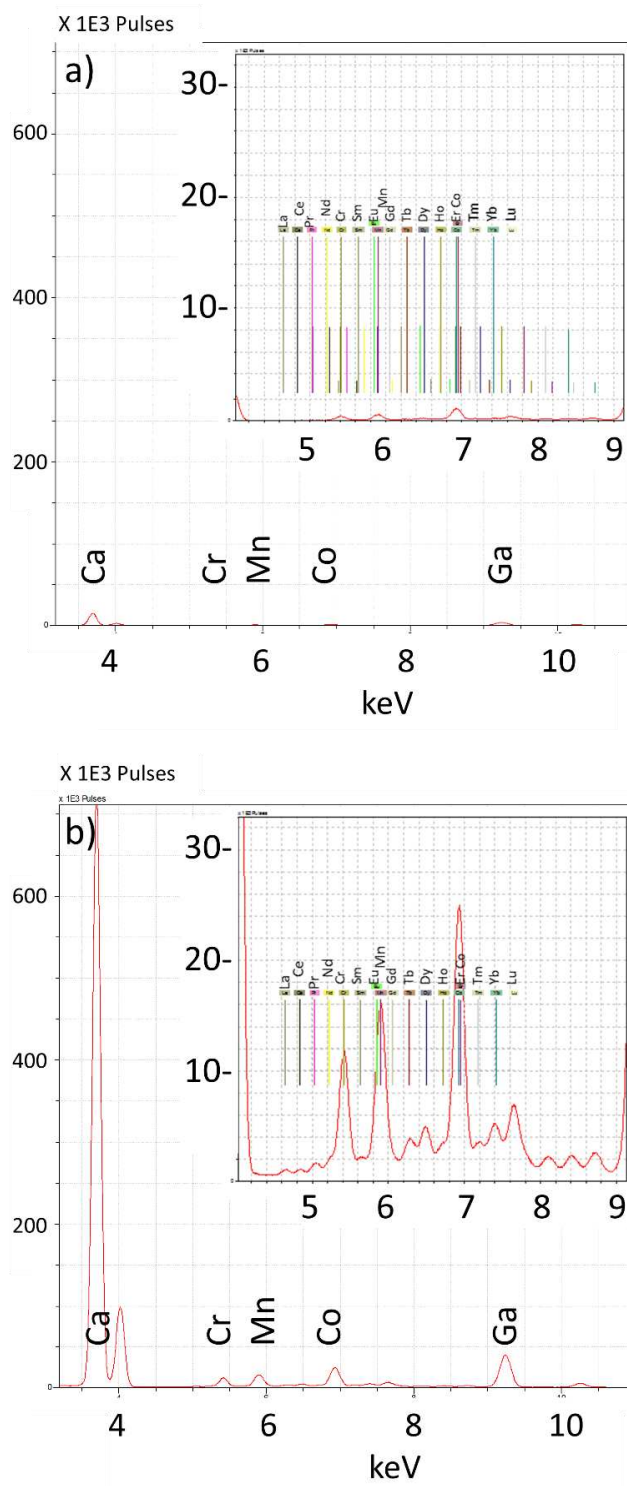
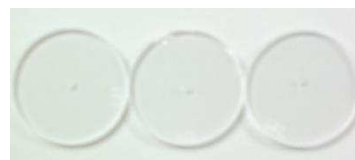
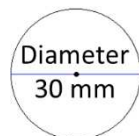
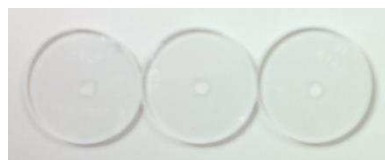


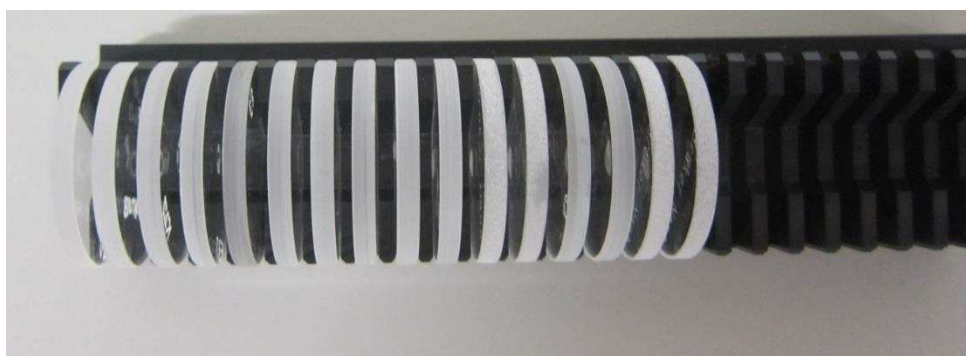
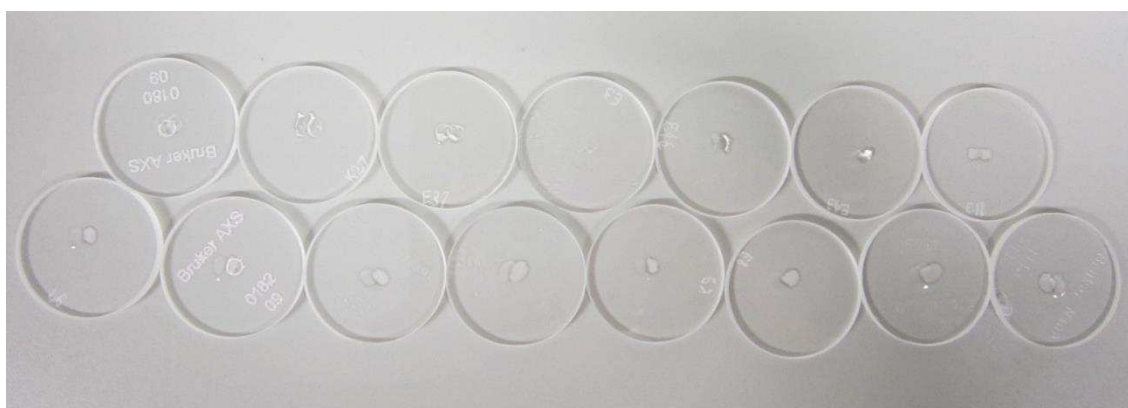
Figure S1. Number of counts depicted in the spectra of the 5  $\mu\text{L}$ -solution sampled on the carrier when dissolving with a) MilliQ water or b) an aqueous solution of Triton<sup>TM</sup> X-100, 53.50  $\text{g L}^{-1}$ . The final composition is 0.005 M of 20 analyte elements with 0.980 molar ratio between the matrix element  $\text{CaCl}_2$  and the analytes (27.75  $\text{g L}^{-1}$  of  $\text{CaCl}_2$ ).

Photos of the carriers after TXRF measurements



a) Solution of 53.5 g L<sup>-1</sup> of Triton™ X-100.

Solution without Triton™ X-100



b) Solution with 53.5 g L<sup>-1</sup> of Triton™ X-100

Figure S2. a) Appearance of the dried 5- $\mu$ L sample deposited on the carriers after TXRF measurements with and without a 53.5 g L<sup>-1</sup> solution of Triton™ X-100 in water. b) The matrix is uniformly distributed over a bigger (top b)) and thinner (bottom b)) surface on the carrier when using Triton™ X-100, obtaining reproducible drops on the carrier.

**Table S1. Recovery rates (average from duplicates) of 20 elements using nine different internal standards with no matrix of CaCl<sub>2</sub>. The solution contains in total 0.005 M of 20 elements from standard solutions: 50 mg L<sup>-1</sup> of Cr, Mn, Co, Ga and Sr, and 10 mg L<sup>-1</sup> of La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu and Y. No Triton™ X-100 was added in the internal standardization.**

Y	Lu	Yb	Tm	Er	Ho	Dy	Tb	Gd	Eu	Sm	Nd	Pr	Ce	La	Sr	Ga	Co	Mn	Cr	←Analyte, X-ray radiation	Internal standard, IS (X-ray radiation) ↓
<i>La</i>	<i>La</i>	<i>La</i>	<i>La</i>	<i>La</i>	<i>La</i>	<i>La</i>	<i>La</i>	<i>La</i>	<i>La</i>	<i>La</i>	<i>La</i>	<i>La</i>	<i>La</i>	<i>La</i>	<i>Kα</i>	<i>Kα</i>	<i>Kα</i>	<i>Kα</i>	<i>Kα</i>		
14.958	7.656	7.416	7.180	6.949	6.720	6.495	6.273	6.057	5.846	5.636	5.2304	5.0337	4.8402	4.65097	14.165	9.25174	6.93032	5.89875	5.41472		
86	90	99	99	99	89	103	92	96	69	108	97	107	91	102	89	97	99	94			Cr (Kα 5.41472)
92	95	105	105	106	94	109	104	100	87	95	109	110	106	103	95	100	106		102		Mn (Kα 5.89875)
90	93	103	103	103	92	106	95	99	72	113	101	111	95	106	92	101		98	105		Co (Kα 6.93032)
90	93	103	103	103	92	107	95	100	72	113	101	112	95	106	93		103	98	105		Ga (Kα 9.25174)
99	103	114	114	114	102	118	105	110	79	124	111	123	105	117		112	114	108	116		Sr (Kα 14.165)
80	83	93	92	92	83	96	85	89	64	101	90		85	95	83	91	92	88	94		Pr (Lα 5.0337)
89	92	102	102	102	91	106	95	99	71	112		111	94	105	92	100	102	97	104		Nd (Lα 5.2304)
97	101	112	112	112		116	103	108	78	122	110	121	103	115	101	110	112	107	114		Ho (Lα 6.720)
87	90	100	100		90	104	93	97	70	110	98	108	92	103	90	98	100	95	102		Er (Lα 6.949)

Average ± standard deviation of all: 99.4 ± 10.7%

n.d., not detected.

Table S2. Recovery rates average from duplicates of 20 elements (50 mg L<sup>-1</sup> of Cr, Mn, Co, Ga and Sr, and 10 mg L<sup>-1</sup> of La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu and Y) using nine of them as internal standards; in a 5.55 g L<sup>-1</sup> CaCl<sub>2</sub> (0.910 mole fraction). No Triton™ X-100 was added in the internal standardization.

Y La 14.958	Lu La 7.656	Yb La 7.416	Tm La 7.180	Er La 6.949	Ho La 6.720	Dy La 6.495	Tb La 6.273	Gd La 6.057	Eu La 5.846	Sm La 5.636	Nd La 5.2304	Pr La 5.0337	Ce La 4.8402	La La 4.65097	Sr Ka 14.165	Ga Ka 9.25174	Co Ka 6.930325	Mn Ka 5.89875	Cr Ka 5.41472	←Analyte, X-ray radiation Internal standard, IS (X-ray adiation)↓
233	191	173	161	182	141	147	121	119	90	137	96	96	75	73	235	200	157	116		Cr (Ka 5.41472)
199	164	150	140	158	123	129	106	104	80	120	85	85	67	65	201	172	137		90	Mn (Ka 5.89875)
145	121	113	106	118	93	98	81	78	62	92	66	66	52	52	146	127		78	69	Co (Ka 6.93032)
113	97	94	88	97	77	82	69	65	54	78	58	58	46	47	114		85	66	60	Ga (Ka 9.25174)
101	88	87	81	89	71	76	64	60	51	73	55	55	44	45		91	79	62	56	Sr (Ka 14.165)
253	205	184	170	195	149	155	128	126	94	144	100		78	74	256	216	167	122	107	Pr (La 5.0337)
253	206	184	171	195	150	156	128	126	94	144		100	78	74	256	216	167	122	107	Nd (La 5.2304)
157	131	122	114	128		105	88	84	67	99	72	71	56	56	159	137	111	84	75	Ho (La 6.720)
121	102	96	90		79	84	70	67	54	79	58	58	46	46	122	106	88	67	60	Er (La 6.949)

Average ± standard deviation of all: 110.6 ± 49.5%

n.d., not detected.

**Table S3. Recovery rates average from duplicates of 20 elements (50 mg L<sup>-1</sup> of Cr, Mn, Co, Ga and Sr, and 10 mg L<sup>-1</sup> of La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu and Y), using nine of them as internal standards; in a 55.49 g L<sup>-1</sup> CaCl<sub>2</sub> (0.990 mole fraction). No Triton™ X-100 was added in the internal standardization.**

	Y <i>La</i>	Lu <i>La</i>	Yb <i>La</i>	Tm <i>La</i>	Er <i>La</i>	Ho <i>La</i>	Dy <i>La</i>	Tb <i>La</i>	Gd <i>La</i>	Eu <i>La</i>	Sm <i>La</i>	Nd <i>La</i>	Pr <i>La</i>	Ce <i>La</i>	La <i>La</i>	Sr <i>Ka</i>	Ga <i>Ka</i>	Co <i>Ka</i>	Mn <i>Ka</i>	Cr <i>Ka</i>	←Analyte, X-ray Radiation	Internal standard, IS (X-ray radiation)↓
	14.958	7.656	7.416	7.180	6.949	6.720	6.495	6.273	6.057	5.846	5.636	5.2304	5.0337	4.8402	4.65097	14.165	9.25174	6.930325	5.89875	5.41472		
820	252	182	255	265	140	71	<b>106</b>	n.d.	143	68	n.d.	n.d.	n.d.	n.d.	1300	624	227	129			Cr (Kα 5.41472)	
649	201	148	205	211	<b>111</b>	57	<b>84</b>	n.d.	<b>105</b>	50	n.d.	n.d.	n.d.	n.d.	1029	495	179		<b>81</b>		Mn (Kα 5.89875)	
371	<b>114</b>	83	<b>116</b>	<b>120</b>	63	32	48	n.d.	62	30	n.d.	n.d.	n.d.	n.d.	587	282		<b>58</b>	46		Co (Kα 6.93032)	
133	41	30	42	43	23	12	17	n.d.	23	11	n.d.	n.d.	n.d.	n.d.	211		<b>37</b>	21	17		Ga (Kα 9.25174)	
<b>64</b>	20	14	20	21	11	6	8	n.d.	11	5	n.d.	n.d.	n.d.	n.d.		<b>49</b>	18	10	8		Sr (Kα 14.165)	
n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	<b></b>	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.		Pr (Lα 5.0337)
n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	<b></b>	<b></b>	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.		Nd (Lα 5.2304)
588	181	131	183	190		<b>51</b>	76	n.d.	<b>103</b>	49	n.d.	n.d.	n.d.	n.d.	931	447	162	93	73		Ho (Lα 6.720)	
311	<b>95</b>	68	<b>96</b>		<b>53</b>	27	40	n.d.	57	27	n.d.	n.d.	n.d.	n.d.	492	236	86	49	38		Er (Lα 6.949)	
Average ± standard deviation of all: 93.9 ± 192.4%																n.d., not detected.						



**Table S4. Recovery rates average from duplicates of 20 elements (50 mg L<sup>-1</sup> of Cr, Mn, Co, Ga and Sr, and 10 mg L<sup>-1</sup> of La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu and Y), using nine of them as internal standards; in a 97.11 g L<sup>-1</sup> CaCl<sub>2</sub> (0.994 mole fraction). No Triton™ X-100 was added in the internal standardization.**

Lu <i>La</i> 7.656	Yb <i>La</i> 7.416	Tm <i>La</i> 7.180	Er <i>La</i> 6.949	Ho <i>La</i> 6.720	Dy <i>La</i> 6.495	Tb <i>La</i> 6.273	Gd <i>La</i> 6.057	Eu <i>La</i> 5.846	Sm <i>La</i> 5.636	Nd <i>La</i> 5.2304	Pr <i>La</i> 5.0337	Ce <i>La</i> 4.8402	La <i>La</i> 4.65097	Sr <i>Ka</i> 14.165	Ga <i>Ka</i> 9.25174	Co <i>Ka</i> 6.93032	Mn <i>Ka</i> 5.89875	Cr <i>Ka</i> 5.41472	Cr <i>Ka</i> 5.41472	←Analyte, X-ray Radiation	Internal standard, IS (X-ray radiation)↓	
424	259	261	179	230	194	163	<b>116</b>	n.d.	<b>91</b>	<b>121</b>	n.d.	n.d.	n.d.	n.d.	1385	628	214	111	■	Cr (Kα 5.41472)		
0	0	0	0	0	0	145	<b>112</b>	n.d.	<b>82</b>	<b>122</b>	n.d.	n.d.	n.d.	0	0	579	197	■	91	Mn (Kα 5.89875)		
203	<b>125</b>	<b>124</b>	<b>84</b>	<b>111</b>	<b>93</b>	80	56	n.d.	45	56	n.d.	n.d.	n.d.	n.d.	663	300	■	53	47	Co (Kα 6.93032)		
<b>68</b>	42	43	29	38	32	27	18	n.d.	15	19	n.d.	n.d.	n.d.	n.d.	224	■	35	18	16	Ga (Kα 9.25174)		
30	19	20	14	19	15	13	8	n.d.	6	8	n.d.	n.d.	n.d.	n.d.	■	47	16	9	7	Sr (Kα 14.165)		
n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	■	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	Pr (Lα 5.0337)	
n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	■	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	Nd (Lα 5.2304)	
227	136	135	<b>93</b>	<b>114</b>	■	<b>83</b>	64	n.d.	48	68	n.d.	n.d.	n.d.	n.d.	728	327	111	58	51	Ho (Lα 6.720)		
821	382	422	388	■	280	71	268	n.d.	39	453	n.d.	n.d.	n.d.	n.d.	2346	995	335	160	152	Er (Lα 6.949)		
Average ± standard deviation of all: 105.0 ± 255.4%															n.d., not detected.							

**Table S5. Recovery rates average from duplicates of 20 elements (50 mg L<sup>-1</sup> of Cr, Mn, Co, Ga and Sr, and 10 mg L<sup>-1</sup> of La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu and Y), using nine of them as internal standards; in a 138.73 g L<sup>-1</sup> CaCl<sub>2</sub> (0.996 mole fraction). No Triton™ X-100 was added in the internal standardization.**

Y	Lu	Yb	Tm	Er	Ho	Dy	Tb	Gd	Eu	Sm	Nd	Pr	Ce	La	Sr	Ga	Co	Mn	Cr	←Analyte, X-ray Radiation	
<i>La</i>	<i>La</i>	<i>La</i>	<i>La</i>	<i>La</i>	<i>La</i>	<i>La</i>	<i>La</i>	<i>La</i>	<i>La</i>	<i>La</i>	<i>La</i>	<i>La</i>	<i>La</i>	<i>La</i>	<i>Ka</i>	<i>Ka</i>	<i>Ka</i>	<i>Ka</i>	<i>Ka</i>	<i>Ka</i>	
14.958	7.656	7.416	7.180	6.949	6.720	6.495	6.273	6.057	5.846	5.636	5.2304	5.0337	4.8402	4.65097	14.165	9.25174	6.930325	5.89875	5.41472	Internal standard, IS (X-ray radiation)↓	
455	241	226	189	n.d.	267	144	<b>105</b>	<b>113</b>	120	n.d.	n.d.	n.d.	160	n.d.	1527	622	223	109	■	Cr (Kα 5.41472)	
0	0	0	0	0	0	<b>113</b>	<b>80</b>	159	<b>94</b>	n.d.	n.d.	n.d.	224	0	0	563	0	■	99	Mn (Kα 5.89875)	
203	109	<b>120</b>	<b>86</b>	n.d.	<b>102</b>	55	43	76	46	n.d.	n.d.	n.d.	<b>107</b>	n.d.	689	283	■	50	49	Co (Kα 6.93032)	
72	39	44	31	n.d.	37	20	14	29	17	n.d.	n.d.	n.d.	41	n.d.	245	■	37	18	18	Ga (Kα 9.25174)	
30	16	19	13	n.d.	16	9	5	13	7	n.d.	n.d.	n.d.	18	n.d.	■	894	15	7	8	Sr (Kα 14.165)	
n.d.	n.d.	n.d.	n.d.	n.d.	■	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	■	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	Pr (Lα 5.0337)
n.d.	n.d.	n.d.	n.d.	■	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	■	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	Nd (Lα 5.2304)
1913	984	809	698	n.d.	n.d.	54	899	336	45	n.d.	n.d.	n.d.	475	n.d.	6736	2581	894	455	401	Ho (Lα 6.720)	
n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	Er (Lα 6.949)

Average ± standard deviation of all: 157.1 ± 599.9%

n.d., not detected.